

efficient in sensor applications because such materials can be processed easily and have desired properties such as high-surface area and controlled porosity resulting in a sensor with increased sensitivity and durability.

Sensitivity is determined by two factors, the rate of gas diffusion and the rate of oxidation. In this two step process, the gas molecules are transported by diffusion to the catalytic layer, and then oxidized. Sol-gel processing provides a way to increase the number of catalytic active sites and thus increase the rate of oxidation for certain specified exhaust gases. However, in the beginning stages of sensor usage, the increased number of catalytic sites may not drastically increase the sensitivity of the sensor. It is believed that initially, once a given amount of active sites are created, the marginal utility of each subsequent active site decreases. One theory is that during this initial period, because of the large number of active sites created, the rate limiting step becomes the rate of gas diffusion and not the rate of oxidation. Nonetheless, over a period of years the number of catalytic sites decreases as a result of poisoning of the catalyst and thermal sintering. Thus by increasing the number of catalytic sites produced, the enhanced level of sensitivity will be sustained over the course of operation. Accordingly, the durability and life of the sensor significantly increases through the use of sol-gel processed catalytic sensors.

It is further believed that the instant solgel technique provides a catalytic layer with an increased number of active catalytic sites compared to those provided from conventional coating systems. This then may allow the formed coating to be thinner, resulting in a catalytic calorimetric sensor having an enhanced sensitivity.

A schematic diagram of a catalytic calorimetric sensor is shown in FIG. 1. It consists of a substrate **30**. On top of this substrate is a layer to measure the temperature **32**. The temperature measuring device which comprises the temperature measuring layer can be selected from the group consisting of a thermocouple, a temperature dependent metal resistor, a temperature dependent semiconductor resistor, a p-n junction semiconductor and a thermopile. This layer can be made by sputtering, screen printing, sol-gel process, etc. Additionally, a catalytic layer **34** is placed on top of the temperature measuring layer to enable the oxidation of combustible gases in the 300°–500° C. temperature range. The substrate should be as thin as possible. The substrate should preferably have a thickness in the range between 500 to 1000 nm. The substrate should also be comprised of materials with a low thermal conductivity, such as a ceramic or a silicon micromachined structure. Examples of suitable ceramic materials include aluminum oxide, silicon oxide, polysilicon, silicon nitride or combinations thereof.

Below we will also discuss the most preferred embodiment, a differential microcalorimeter structure as shown in FIGS. 2 and 3. It is a differential microcalorimeter in which one membrane is covered with a catalytic layer and the other membrane acts as a reference to compensate for temperature fluctuations in the gas. FIG. 2 is a perspective view of one embodiment of a catalytic differential calorimetric sensor having a silicon frame **40** with two membranes **44** and **45** with temperature measuring layers **48** and **49** placed on top of the membrane. The temperature measuring layers are covered by a passivation layer **41**. A catalytic layer **46** is placed on top of membrane **45**. The temperature measuring layer **49** on membrane **44** is used to measure the temperature of the surrounding gas, while the temperature measuring layer on membrane **45** measures the additional

heat generated by the catalytic layer. Both membranes are thermally insulated from each other, because both membranes have a low thermal conductivity. A cross-sectional view of the sensor of FIG. 2 taken along lines 4–4 is shown in FIG. 3. The various methods of operating differential calorimetric sensors are known and have been described in, for example, *CALORIMETRY FUNDAMENTALS AND PRACTICE* by W. Hemminger (1984), herein incorporated by reference.

The membranes **44** and **45** can be made of silicon nitride. The preferred embodiment includes membranes made of a composite of silicon nitride and silicon oxide layers, most preferably silicon nitride, silicon oxide and silicon nitride layers.

Aluminum oxide can be deposited on top of the membrane structure to improve the adhesive properties of the catalytic layer on the membrane. The resultant membranes have a low thermal conductivity and are tensile so they stay flat over a wide temperature range without buckling.

Although microfabricated catalytic microcalorimeters (FIGS. 2 and 3) are known, the present invention provides a chemical and more effective means of fabrication using the sol-gel process. Metals are traditionally loaded on the membrane by sputtering; however, this technique can produce only a limited number of active sites for catalytic oxidation of the combustible gas molecules. This limited number of active catalytic sites might reduce the sensitivity of a catalytic calorimetric gas sensor. To increase the sensitivity and durability of the sensor for automotive applications, this invention describes sol-gel methods which increase the number of catalytic sites without increasing the size of the device. The number of catalytic sites are increased by the use of sol-gel processed alumina/silica based materials which provide a high-surface area washcoat having controlled porosity with narrow pore-size distribution.

In addition to the sol-gel processed washcoat, the present invention discloses a method to maximize deposition of the catalytically active metal particles in the pores of the washcoat. This method reduces agglomeration of the metal particles available for catalytic reactions. Accordingly, the present invention directed efforts to preparing controlled, small metal particles, using a technique disclosed by Schmid in *Chem. Rev.* 92 (1992) 1709–1727. With Schmid's technique, small noble particles were stabilized by small organic molecules such as sulfanilic acid salts. Another method for preparing controlled size catalytically active metals includes impregnation, whereby the particles are prepared on the washcoat itself. These small noble metal particles in conjunction with high-surface area alumina-based membranes provide a substantially larger number of catalytic sites for calorimetric sensors as compared to conventional fabrication routes.

As used herein, the term washcoat refers to the supporting material on which the catalytically active metal particles are loaded. The term substrate refers to the material supporting the temperature measuring layer and the catalytic layer. The substrate is generally a ceramic **30** or a silicon micromachined structure consisting of a silicon frame **40** and membranes **44** and **45**.

There are several metals which act as catalytically active metals, including but not limited to Fe, Cu, Co, Cr, Ni, Mn, Zn, Cd and Ag and mixtures thereof; however, the preferred active metals are generally noble metals. Noble metals are preferred in large part due to their stability towards catalyst poisons. Noble metals include but are not limited to platinum, palladium, silver, gold, ruthenium, rhodium, osmium, iridium and mixtures thereof.